

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
21 November 2002 (21.11.2002)

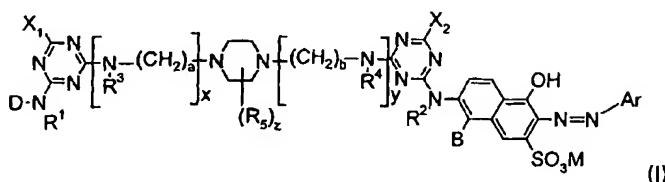
PCT

(10) International Publication Number
WO 02/092697 A1

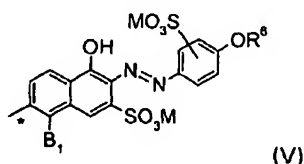
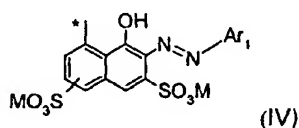
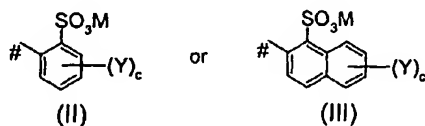
- (51) International Patent Classification⁷: C09B 62/04 // 62/09
- (72) Inventor; and
(75) Inventor/Applicant (for US only): EBENEZER, Warren, James [GB/GB]; 28 Colwyn Road, Bramhall, Stockport, Cheshire SK7 2JA (GB).
- (21) International Application Number: PCT/EP02/04908
- (22) International Filing Date: 4 May 2002 (04.05.2002)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data: 0111573.2 11 May 2001 (11.05.2001) GB
- (71) Applicant (for all designated States except US): DYSTAR TEXTILFARBEN GMBH & CO. DEUTSCHLAND KG [DE/DE]; Eschenheimer Tor 2, 60318 Frankfurt am Main (DE).
- (81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.
- (84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent

[Continued on next page]

(54) Title: FIBRE REACTIVE SCARLET AZO DYES



(57) Abstract: The present invention refers to dyestuffs of the formula I wherein Ar is a group of the formula II or of the formula III, D is a group of the formula IV, or of the formula V wherein the variables are defined as given in claim 1, processes for their preparation and their use for dyeing and printing hydroxy- and/or carboxamido-containing fibre materials.





(BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

Published:

- *with international search report*
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

Description

5 Fibre Reactive Scarlet Azo Dyes

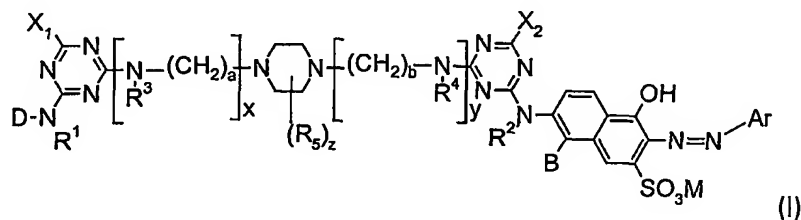
The present invention relates to the field of fibre-reactive dyes.

Dyestuffs containing chromophores linked via a piperazine type linking unit are
 10 known from literature and are described for example in EP-A-0126265, EP-A-0693538 and WO99/05224.

The inventor of the present invention has surprisingly found that dyestuffs with
 a very strong and economic scarlet shade exhibiting excellent fastness properties
 15 can be obtained if piperazine type linking units are used to link two different
 chromophores each selected from a specific range of chromophores as defined
 below.

The present invention claims dyestuffs of the formula I

20



wherein

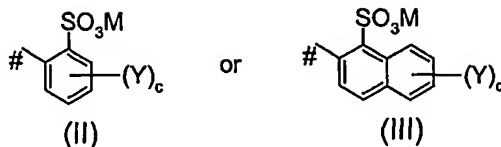
each of R^1 , R^2 , R^3 , R^4 and R^5 , independently, is H or an optionally substituted
 25 alkyl group;

each of X_1 and X_2 , independently, is a labile atom or group;

B is H or SO_3M ;

M is H, an alkali metal, an ammonium ion or the equivalent of an alkaline earth
 metal;

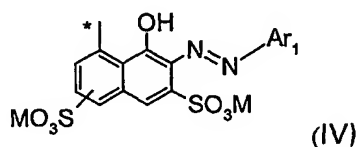
Ar is a group of the formula II or of the formula III



wherein

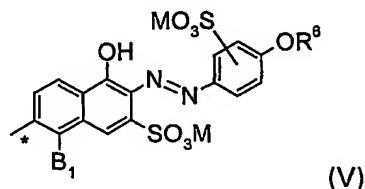
- 5 Y is SO_3M or an alkyl group, c is 0, 1 or 2, M is defined as given above and # indicates the bond to the azo group in formula I;

D is a group of the formula IV



- wherein Ar_1 is defined as Ar, M is defined as given above and * indicates the
10 bond to the NR^1 group of formula I; or

D is a group of the formula V



wherein R^6 is an alkyl group, B_1 is defined as B and M and * are defined as given above;

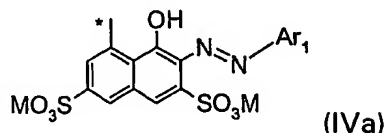
- 15 each of x and y, independently, is 0 or 1 and at least one of x and y is 1;
each of a and b is 2 to 5 and when each of x and y is 1, $a > b$; and
z is 0, 1, 2, 3 or 4.

- Alkyl groups may be straight-chain or branched and are preferably $(\text{C}_1\text{-C}_4)$ -alkyl
20 groups, for example methyl, ethyl, n-propyl, i-propyl or n-butyl. Substituted alkyl groups are preferably substituted by hydroxyl, $(\text{C}_1\text{-C}_4)$ -alkoxy, halogen or carboxyl groups.

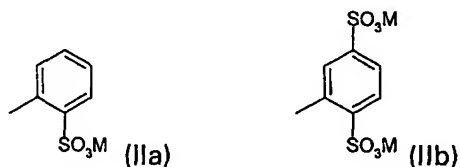
- R^1 to R^6 are preferably H or methyl. R^3 , R^4 and R^5 are especially preferably H.
 X_1 and X_2 are preferably halogen like fluorine and chlorine and are especially
25 preferably chlorine.

M is preferably H, an alkaline metal, like sodium, potassium and lithium and is especially preferably sodium.

D is preferably a group of the formula IVa



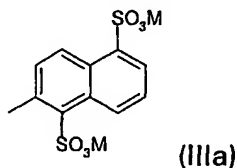
- 5 wherein M, Ar₁ and * are defined as given above. D is especially preferably a group of the formula IVa wherein Ar₁ is a group of the formula IIa or IIb



wherein M is defined as given above.

- If D is a group of the formula IVa with Ar₁ = a group of the formula IIa or IIb, R¹ is preferably H.

Ar is preferably a group of the formula IIIa

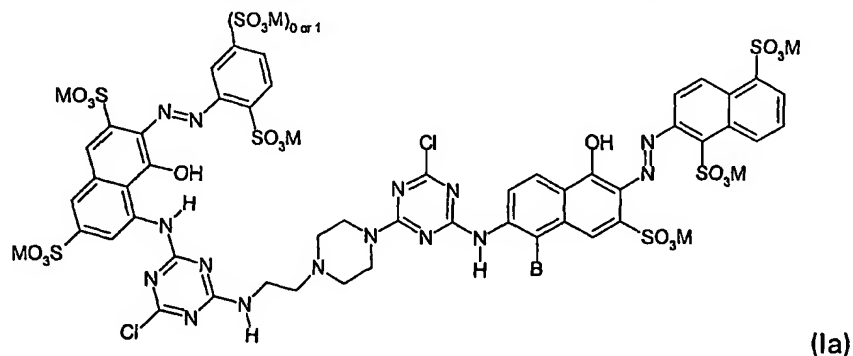


wherein M is defined as given above.

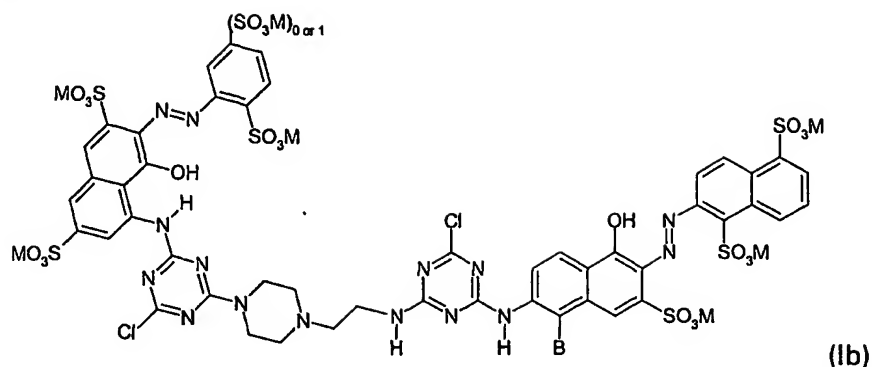
- If Ar is a group of the formula IIIa, R² is preferably H or methyl. If Ar is a group of the formula IIIa, R² and B are especially preferably H.

In preferred dyestuffs of the formula I x = 1 and y = 0 and a = 2 or x = 0 and y = 1 and b = 2.

Especially preferred dyestuffs of the formula I are the dyestuffs of the formula Ia



and of the formula Ib



wherein B and M are defined as given above.

5

The dyestuffs of the present invention can be present as a preparation in solid or liquid (dissolved) form. In solid form they generally contain the electrolyte salts customary in the case of water-soluble and in particular fibre-reactive dyes, such as sodium chloride, potassium chloride and sodium sulfate, and also the auxiliaries customary in commercial dyes, such as buffer substances capable of establishing a pH in aqueous solution between 3 and 7, such as sodium acetate, sodium borate, sodium bicarbonate, sodium citrate, sodium dihydrogenphosphate and disodium hydrogenphosphate, small amounts of siccatives or, if they are present in liquid, aqueous solution (including the presence of thickeners of the type customary in print pastes), substances which ensure the permanence of these preparations, for example mold preventatives.

10
15

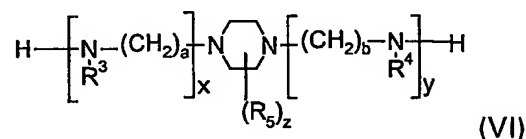
In general, the dyestuffs of the present invention are present as dye powders containing 10 to 80% by weight, based on the dye powder or preparation, of a strength-standardizing colorless diluent electrolyte salt, such as those mentioned above. These dye powders may additionally include the aforementioned buffer substances in a total amount of up to 10%, based on the dye powder. If the dye mixtures of the present invention are present in aqueous solution, the total dye content of these aqueous solutions is up to about 50 % by weight, for example between 5 and 50% by weight, and the electrolyte salt content of these aqueous solutions will preferably be below 10% by weight, based on the

20
25

aqueous solutions. The aqueous solutions (liquid preparations) may include the aforementioned buffer substances in an amount which is generally up to 10% by weight, for example 0.1 to 10% by weight, preference being given to up to 4% by weight, especially 2 to 4% by weight.

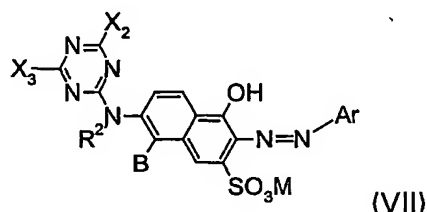
5

A dyestuff of the formula I may for example be prepared by reacting a piperazine compound of the formula VI

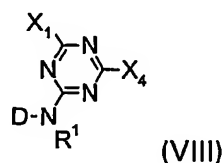


10

wherin R^3 , R^4 , R^5 , a , b , x , y , and z are defined as given above, with a compound of the formula VII



wherein B , M , R^2 , X_2 and Ar are defined as given above and X_3 is a labile atom or a group capable of reaction with an amine, preferably chlorine, and with a compound of the formula VIII

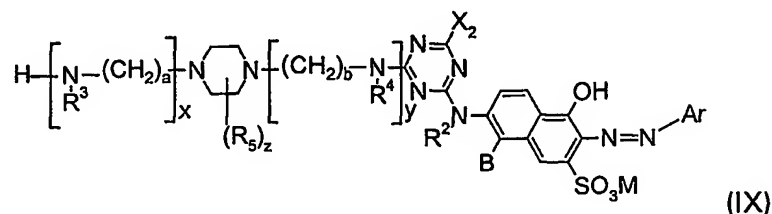


15

wherein D , R^1 and X_1 defined as given above and X_4 has one of the meanings of X_3 .

It is possible to react a compound of formula VI first with a compound of the formula VII to form a compound of the formula IX

20

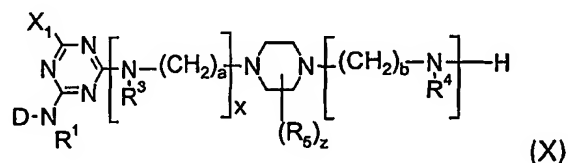


wherein all variables are defined as given above,

which is then reacted with a compound of the formula VIII to a dyestuff of the formula I.

As an alternative is it also possible to react a compound of the formula VI first

5 with a compound of the formula VIII to form the compound of the formula X



wherein all variables are defined as given above,

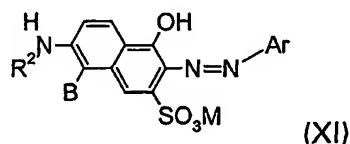
which is then reacted with a compound of the formula VII to a dyestuff of the formula I.

10 In general, one mole of a compound of the formula VI is reacted with 1 mole of a compound of the formula VII and 1 mole of a compound of the formula VIII in a manner known per se to a skilled person.

The compounds of the formulae VI, VII and VIII are known or can easily be

15 prepared by a skilled person using methods which are known per se.

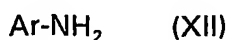
As an example, a compound of the formula VII, wherein X₂ is chlorine can be obtained by reacting cyanuric chloride with a compound of the formula XI



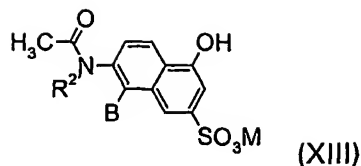
20 wherein B, M, R² and Ar are defined as given above.

The compound of the formula XI can be prepared by means of customary diazotization and coupling reactions in a manner familiar to those skilled in the art using a diazotized amine of the formula XII

25



and a coupling component of the formula XIII



wherein Ar, B, M and R² are defined as given above and subsequently removing the acetyl group (-COCH₃) by saponification.

- 5 The dyestuffs of the instant invention are suitable for dyeing and printing hydroxy- and/or carboxamido-containing fibre materials by the application and fixing methods numerouslly described in the art for fibre-reactive dyes, in scarlet to mid-red shades with good aqueous solubility, color build-up, wash off and robustness to process variables. Moreover, the dyeings obtained surprisingly
10 show very good lightfastness properties.

The present invention therefore also provides for use of the inventive dyestuffs for dyeing and printing hydroxy- and/or carboxamido-containing fibre materials and processes for dyeing and printing such materials using a dyestuff according
15 to the invention. Usually the dyestuff is applied to the substrate in dissolved form and fixed on the fibre by the action of an alkali or by heating or both.

Hydroxy-containing materials are natural or synthetic hydroxy-containing materials, for example cellulose fibre materials, including in the form of paper, or
20 their regenerated products and polyvinyl alcohols. Cellulose fibre materials are preferably cotton but also other natural vegetable fibres, such as linen, hemp, jute and ramie fibres. Regenerated cellulose fibres are for example staple viscose and filament viscose.

25 Carboxamido-containing materials are for example synthetic and natural polyamides and polyurethanes, in particular in the form of fibres, for example wool and other animal hairs, silk, leather, nylon-6,6, nylon-6, nylon-11, and nylon-4.

Application of the inventive dyestuffs is by generally known processes for dyeing and printing fiber materials by the known application techniques for fibre-reactive dyes. The dyestuffs according to the invention are highly compatible with similiar dyes designed for high temperature (80-100°C) applications and are advantageously useful in exhaust dyeing processes.

Similarly, the conventional printing processes for cellulose fibres, which can either be carried out in single-phase, for example by printing with a print paste containing sodium bicarbonate or some other acid-binding agent and the colorant, and subsequent steaming at appropriate temperatures, or in two phases, for example by printing with a neutral or weakly acid print paste containing the colorant and subsequent fixation either by passing the printed material through a hot electrolyte-containing alkaline bath or by overpadding with an alkaline electrolyte-containing padding liquour and subsequent batching of this treated material or subsequent steaming or subsequent treatment with dry heat, produce strong prints with well defined contours and a clear white ground. Changing fixing conditions has only little effect on the outcome of the prints. Not only in dyeing but also in printing the degrees of fixation obtained with dye mixtures of the invention are very high. The hot air used in dry heat fixing by the customary thermofix processes has a temperature of from 120 to 200°C. In addition to the customary steam at from 101 to 103°C, it is also possible to use superheated steam and high pressure steam at up to 160°C.

The inventive dyestuffs can in addition be used to produce inks useful for printing the substrates described above, for example textiles, especially cellulosic textiles, and paper. Such inks can be used in all technologies, for example conventional printing, ink-jet printing or bubble-jet printing (for information on such printing technologies see for example Text. Chem. Color, Volume 19(8), pages 23 ff and Volume 21, pages 27 ff).

Acid-binding agents responsible for fixing the dyes to cellulose fibres are for example water-soluble basic salts of alkali metals and of alkaline earth metals of inorganic or organic acids, and compounds which release alkali when hot. Of

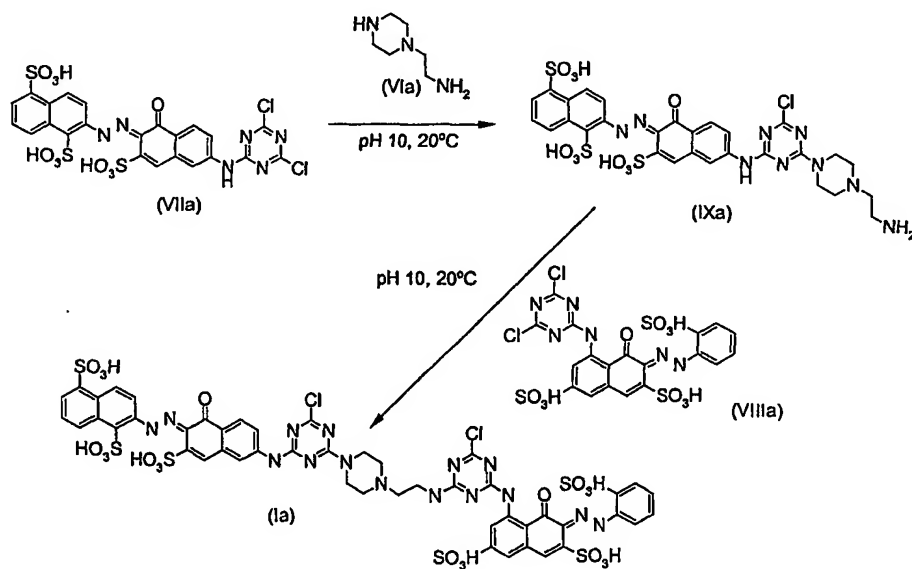
particular suitability are the alkali metal hydroxides and alkali metal salts of weak to medium inorganic or organic acids, the preferred alkali metal compounds being the sodium and potassium compounds. These acid-binding agents are for example sodium hydroxide, potassium hydroxide, sodium carbonate, sodium bicarbonate, potassium carbonate, sodium formate, sodium dihydrogenphosphate and disodium hydrogenphosphate.

Treating the dyestuffs according to the invention with the acid-binding agents with or without heating bonds the dyes chemically to the cellulose fibre. Especially the dyeings on cellulose, after they have been given the usual aftertreatment of rinsing to remove unfixed dye portions, show excellent properties.

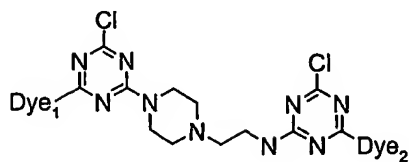
The dyeings of polyurethane and polyamide fibres are customarily carried out from an acid medium. The dyebath may contain for example acetic acid and/or ammonium sulfate and/or acetic acid and ammonium acetate or sodium acetate to bring it to the desired pH. To obtain a dyeing of acceptable levelness it is advisable to add customary leveling auxiliaries, for example based on a reaction product of cyanuric chloride with three times the molar amount of an aminobenzenesulfonic acid or aminonaphthalenesulfonic acid or based on a reaction product of for example stearylamine with ethylene oxide. In general the material to be dyed is introduced into the bath at a temperature of about 40°C and agitated therein for some time, the dyebath is then adjusted to the desired weakly acid, preferably weakly acetic acid, pH, and the actual dyeing is carried out at temperature between 60 and 98°C. However, the dyeings can also be carried out at the boil or at temperatures up to 120°C (under superatmospheric pressure).

Example 1

1-(2-aminoethyl) piperazine (IVa) (1.3g, 0.01 mol) was added dropwise to a stirred suspension of the orange dichlorotriazinyl dye (VIIa) (0.01 mol) in water (400 mls) at ambient temperature and pH6. The pH was then adjusted to 10 with sodium hydroxide solution and maintained at this pH for 30 minutes, yielding a slurry of the orange dye (IXa). To this suspension was added the red dichlorotriazinyl dye (VIIIa) (13.56g, 0.01 mol) and the solution was maintained at pH 10 and ambient temperature overnight. The pH was adjusted to 6 with 2N HCl and the dye precipitated by the addition of methylated spirit. The precipitated dye was filtered off and dried to give the expected dye (Ia) (12.5g). ($\lambda_{\max} = 510\text{nm}$, $\epsilon = 76000$, $\nu_{\text{max}} = 102\text{nm}$). Other analytical data were in full agreement with the expected structure.

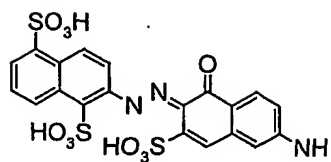


Following exactly analogous procedures the following dyes (examples 2 – 17) were synthesised.

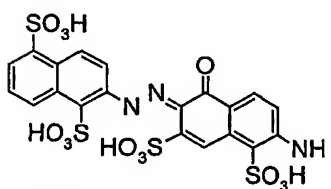


5

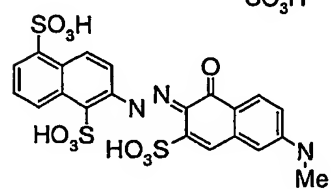
Example	Dye 1	Dye 2	λ max/nm
2	e	d	506
3	h	d	511
4	e	a	508
5	c	e	510
6	a	f	513
7	c	f	514
8	a	g	514
9	e	b	508
10	b	f	513
11	a	h	513
12	c	h	514
13	b	h	513
14	h	b	512
15	b	e	509
16	i	a	506
17	a	i	508
18	c	j	511



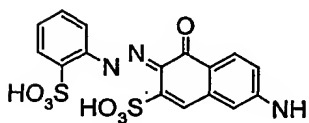
a



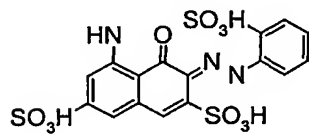
b



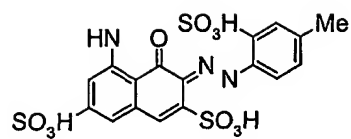
c



d



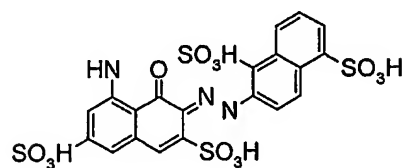
e



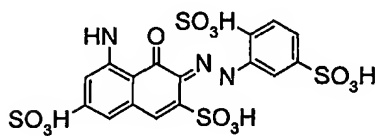
f



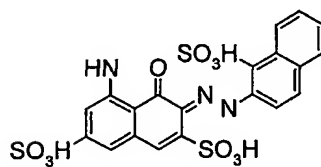
g



h



i



j

5

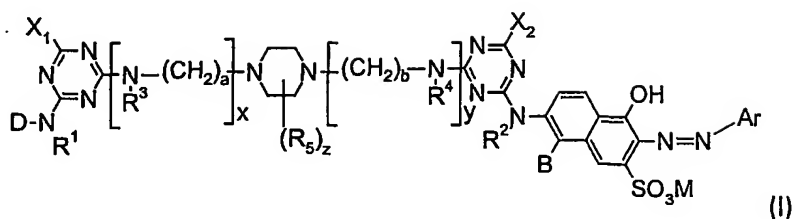
10

15

20

Claims

1. A dyestuff of the formula I



wherein

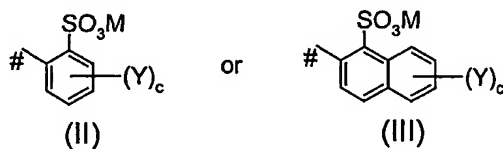
each of R¹, R², R³, R⁴ and R⁵, independently, is H or an optionally substituted alkyl group;

each of X₁ and X₂, independently, is a labile atom or group;

B is H or SO₃M;

M is H, an alkali metal, an ammonium ion or the equivalent of an alkaline earth metal;

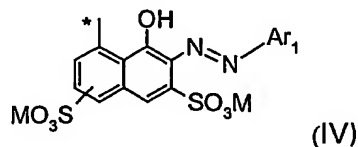
Ar is a group of the formula II or of the formula III



wherein

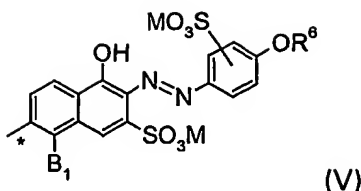
Y is SO₃M or an alkyl group, c is 0, 1 or 2, M is defined as given above and # indicates the bond to the azo group in formula I;

D is a group of the formula IV



wherein Ar₁ is defined as Ar, M is defined as given above and * indicates the bond to the NR¹ group of formula I; or

D is a group of the formula V



wherein R^6 is an alkyl group, B_1 is defined as B and M and * are defined as given above;

each of x and y, independently, is 0 or 1 and at least one of x and y is 1;

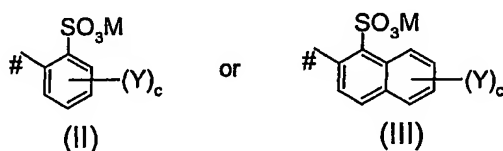
5 each of a and b is 2 to 5 and when each of x and y is 1, $a > b$; and
z is 0, 1, 2, 3 or 4.

2. A dyestuff as claimed in claim 1, wherein X_1 and X_2 are halogen, preferably chlorine.

10

3. A dyestuff as claimed in claim 1 and/or 2, wherein M is H or an alkaline metal, preferably sodium.

4. A dyestuff as claimed in one or more of claims 1 to 3, wherein Ar is a group
15 of the formula II or of the formula III



wherein

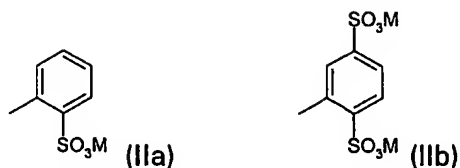
Y is SO_3M or an alkyl group, c is 0, 1 or 2, M is defined as given in claim 1 and #
20 indicates the bond to the azo group in formula I.

5. A dyestuff as claimed in one or more of claims 1 to 4, wherein D is a group of the formula IVa



25 wherein M, Ar_1 and * are defined as given in claim 1.

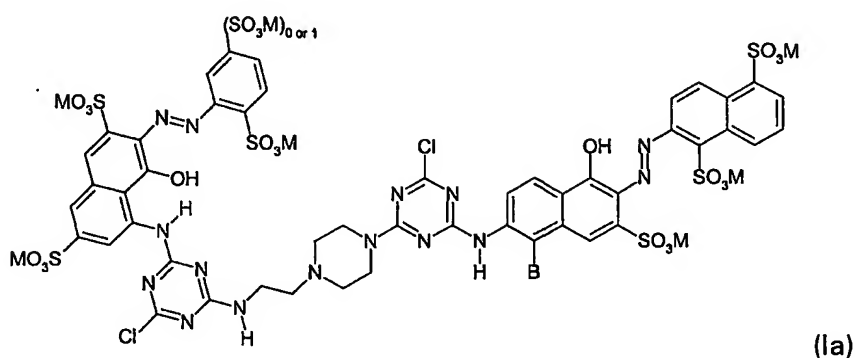
6. A dyestuff as claimed in claim 5, wherein Ar₁ is a group of the formula IIa or IIb



wherein M is defined as given in claim 1.

5

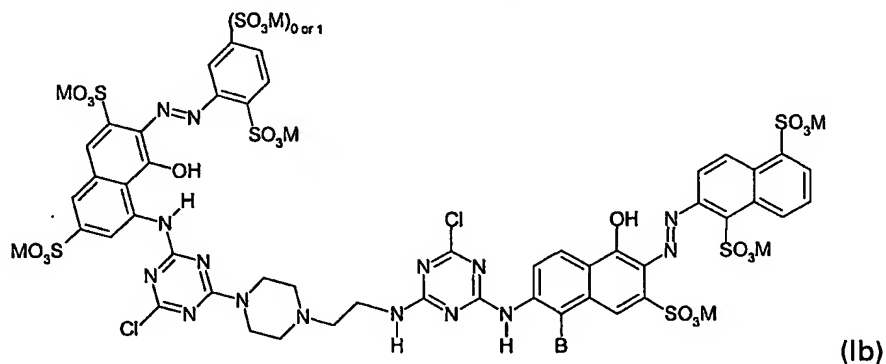
7. A dyestuff as claimed in one or more of claims 1 to 6 of the formula Ia



wherein B and M are defined as given in claim 1.

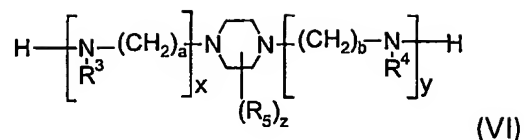
10

8. A dyestuff as claimed in one or more of claims 1 to 6 of the formula Ib

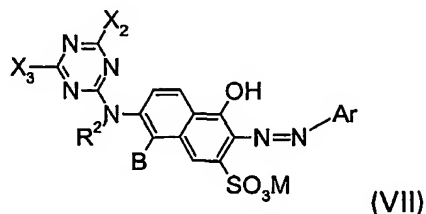


wherein B and M are defined as given in claim 1.

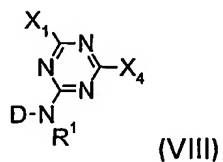
15 9. A process for preparing a dyestuff of formula I as claimed in one or more of claims 1 to 8 by reacting a piperazine compound of the formula VI



wherein R^3 , R^4 , R^5 , a , b , x , y , and z are defined as given in claim 1, with a compound of the formula VII



- 5 wherein B , M , R^2 , X_2 and Ar are defined as given in claim 1 and X_3 is a labile atom or a group capable of reaction with an amine, preferably chlorine, and with a compound of the formula VIII



- wherein D , R^1 and X_1 defined as given in claim 1 and X_4 has one of the meanings
10 of X_3 .

10. A process for dyeing and printing hydroxy- and/or carboxamido-containing fibre materials in which a dyestuff of the formula I according to one or more of claims 1 to 8 is used.

INTERNATIONAL SEARCH REPORT

International Application No.

PCT/EP 04908

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C09B62/04 //C09B62/09

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

PAJ, EP0-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 99 05224 A (BASF AG ;EBENEZER WARREN JAMES (GB); MYNETT DONNA MARIA (GB)) 4 February 1999 (1999-02-04) cited in the application page 13, line 17 -page 16, last line page 2, line 4 -page 3, line 11 page 25, line 19 -page 26, line 12	1-10
Y	WO 00 36025 A (CLARIANT FINANCE BVI LTD ;CLARIANT INT LTD (CH)) 22 June 2000 (2000-06-22) example 21	1-10
Y	US 3 647 778 A (ANDREW HERBERT FRANCIS ET AL) 7 March 1972 (1972-03-07) claims 1,4,5; examples 15-22,43-50,55-59,75-84,87-96	1-10

☐ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the International filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the International search

15 October 2002

Date of mailing of the International search report

22/10/2002

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Ginoux, C

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No.

PCT/EP/04908

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 9905224	A	04-02-1999	BR 9811035 A CN 1265129 T DE 69804105 D1 EP 0998531 A1 WO 9905224 A1 JP 2001510875 T TR 200000227 T2 US 6248871 B1	01-08-2000 30-08-2000 11-04-2002 10-05-2000 04-02-1999 07-08-2001 21-09-2000 19-06-2001
WO 0036025	A	22-06-2000	AU 1403500 A BR 9916026 A EP 1137715 A1 WO 0036025 A1 TR 200101635 T2 US 6319290 B1	03-07-2000 04-09-2001 04-10-2001 22-06-2000 22-10-2001 20-11-2001
US 3647778	A	07-03-1972	CH 542268 A CH 541610 A CH 541611 A CS 178065 B2 CS 178098 B2 CS 178099 B2 DE 2001960 A1 ES 375496 A1 ES 378464 A1 ES 378465 A1 FR 2028479 A5 GB 1283771 A NL 7000663 A , B PL 80765 B1	30-09-1973 31-10-1973 31-10-1973 31-08-1977 31-08-1977 31-08-1977 30-07-1970 16-05-1972 16-06-1972 16-06-1972 09-10-1970 02-08-1972 20-07-1970 30-08-1975